



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number : **0 390 083 B1**

⑫

EUROPEAN PATENT SPECIFICATION

④⑤ Date of publication of patent specification :
03.11.93 Bulletin 93/44

⑤① Int. Cl.⁵ : **C08G 77/38, C08G 77/44,**
C08G 77/18, C08L 83/06

②① Application number : **90105834.7**

②② Date of filing : **27.03.90**

⑤④ **Liquid silicone resin compositions.**

The file contains technical information
submitted after the application was filed and
not included in this specification

③⑦ Priority : **28.03.89 US 329911**

④③ Date of publication of application :
03.10.90 Bulletin 90/40

④⑤ Publication of the grant of the patent :
03.11.93 Bulletin 93/44

⑥④ Designated Contracting States :
BE DE FR GB

⑤⑥ References cited :
DD-A- 137 720
US-A- 2 909 549
US-A- 4 448 927

⑦③ Proprietor : **DOW CORNING CORPORATION**
P.O. Box 1767
Midland Michigan 48686-0994 (US)

⑦② Inventor : **Fillmore, Danielle Marie**
5070 Hope Road
Hope, Michigan (US)
Inventor : **Swihart, Terence John**
1544 St. Mary
Essexville, Michigan (US)
Inventor : **Price, John Geoffrey, Samy**
Maes-y-Coed, The Knap
Barry CF6 8SZ, South Glamorgan, Wales (GB)

⑦④ Representative : **Spott, Gottfried, Dr. et al**
Patentanwälte Spott und Puschmann
Sendlinger-Tor-Platz 11
D-80336 München (DE)

EP 0 390 083 B1

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

The present invention relates to a liquid silicone resin composition. More particularly, the present invention relates to a solventless silicone resin which is prepared by partially hydrolyzing a mixture of a polydimethylsiloxane and a methyltrialkoxysilane, using a perfluoroalkane sulfonic acid as an equilibrating catalyst.

Silicone resins having trifunctional siloxy units and difunctional siloxy units are well known in the art and have been used extensively in the formulation of paints, varnishes, molding compounds and encapsulating compositions. Typically, these resins contain residual hydroxyl functionality, and occasionally residual alkoxy functionality, which may be condensed by means of heat and/or catalysis in order to cure the resins. Resins of this type are generally utilized in the form of solutions in organic solvents since they are often solids, or, at best, very viscous liquids at ordinary temperatures.

DD-A 137 720 discloses a liquid silicone resin composition prepared by a process comprising reacting a mixture of cyclic polydimethylsiloxane, methyltriethoxysilane and an equilibrating amount of a basic catalyst, hydrolyzing the reaction product with water and an equilibrating amount of a basic catalyst, hydrolyzing the reaction product with water to provide residual alkoxy functionality and neutralizing the basic catalyst with CO_2 . With this process, a residual ethoxy functionality of the resin of at least 11.10% is obtained. Moreover, the gel time of the resins is relatively high.

Prior to our discovery, we believe that no one has taught the preparation of stable, low viscosity, alkoxy-functional, 100% reactive silicone resins prepared according to the method of the present invention. Moreover, it has been discovered that the resins prepared according to the methods of the present invention may be modified with both traditional phenyl-containing silanol-functional solid resins as well as with polydimethylsiloxane fluids, the latter addition imparting increased slip to the cured resin.

Additionally, the resins prepared according to the method of the present invention rely on methyltrialkoxysilanes as starting materials. These methyltrialkoxysilanes can be readily obtained in purified form by distillation and the resulting resins are therefore relatively free of the residual chlorine contamination generally found in resins prepared from chlorosilanes. This often translates into reduced corrosion of metal surfaces coated with the resins and can be a particularly significant advantage in electronic applications.

The present invention therefore relates to a liquid silicone resin composition prepared by a process comprising:

- (I) reacting a mixture consisting essentially of
 - (A) a polydimethylsiloxane, wherein optionally up to 10 mole percent of siloxane units may contain alkyl groups having 2 to 8 carbon atoms, phenyl groups or trifluoropropyl groups,
 - (B) a methyltrialkoxysilane having the formula $\text{MeSi}(\text{OR})_3$, wherein Me denotes a methyl radical and R is an alkyl radical having from 1 to 3 carbon atoms, and
 - (C) an equilibrating amount of an acid catalyst having the formula $\text{R}'\text{SO}_3\text{H}$ wherein R' is a perfluoroalkyl group having 1 to 10 carbon atoms, the molar ratio of said methyltrialkoxysilane (B) to said polydimethylsiloxane (A) being between 1:1 and 10:1;
- (II) hydrolyzing the reaction product formed in step (I) with sufficient water to provide from 0.48 to 0.81 moles of residual alkoxy functionality per 100 parts by weight of said liquid silicone resin; and
- (III) neutralizing said acid catalyst (C).

The present invention further relates to a liquid resin composition prepared by a process comprising reacting the above mentioned components (A), (B) and (C) in the presence of a sufficient quantity of water of hydrolysis to provide from 0.48 to 0.81 moles of residual alkoxy functionality per 100 parts by weight of said liquid silicone resin and neutralizing the acid catalyst (C).

The present invention still further relates to the above described processes used to make the liquid silicone resin compositions.

The polydimethylsiloxane (A) of the liquid silicone resin composition may be a linear polydimethylsiloxane. The selection of terminal groups for the polydimethylsiloxane is not being critical for the purpose of the present invention provided that an inert terminal group, such as trimethylsilyl, is not employed when the degree of polymerization of the polydimethylsiloxane is less than about 200. Thus, generic examples of suitable terminal groups include trialkylsilyl, alkoxydialkylsilyl, aryldialkylsilyl and hydroxydialkylsilyl groups. Specific terminal groups which may be used include $\text{Me}_3\text{Si}-$, $\text{MeO}(\text{Me}_2)\text{Si}-$ and $\text{HO}(\text{Me}_2)\text{Si}-$, wherein Me hereinafter denotes a methyl radical. Preferably, the end group is $\text{HO}(\text{Me}_2)\text{Si}-$.

Although component (A) is described as a polydimethylsiloxane, up to about 10 mole percent of siloxane units containing alkyl groups having 2 to 8 carbon atoms, phenyl groups or trifluoropropyl groups may be copolymerized with the dimethylsiloxane units to still be within the scope of this invention. Thus, copolymers of dimethylsiloxane units with phenylmethylsiloxane, methylhexylsiloxane or methyltrifluoropropylsiloxane units are specific examples of this component. It is preferred that when component (A) is a linear polydimethylsi-

loxane, that it be the dimethyl homopolymer.

Alternatively, and preferably, polydimethylsiloxane (A) is selected from at least one polydimethylcyclodioxane having the formula $(\text{Me}_2\text{SiO})_x$ wherein x is an integer between 3 and 10, inclusive. For the purposes of the present invention, this preferred polydimethylsiloxane is a mixture of such cyclic siloxanes.

Component (B) of the present invention may be represented by the formula $\text{MeSi}(\text{OR})_3$ wherein R is independently selected from alkyl radicals having from 1 to 3 carbon atoms. The preferred alkoxy silane is methyltrimethoxysilane.

The acid catalyst (C) may be represented by the general formula $\text{R}'\text{SO}_3\text{H}$ wherein R' is a perfluoroalkyl group having 1 to about 10 carbon atoms. Examples of suitable acid catalysts include perfluoromethane sulfonic acid, perfluoroethane sulfonic acid, perfluorohexane sulfonic acid, perfluorooctane sulfonic acid and perfluorodecane sulfonic acid. Component (C) is a strong acid capable of efficiently redistributing (i.e., equilibrating) siloxane bonds and is preferably perfluoromethane sulfonic acid. It has been observed that weaker acids, such as phosphoric or acetic acid, do not redistribute siloxane bonds and therefore do not produce the liquid silicone resins of the present invention.

All the components of the present invention are well known in the art and many are available commercially, so that no further description thereof is considered necessary.

In order to prepare the liquid silicone resin compositions of the present invention, from about 1 to about 10 moles of methyltrialkoxysilane (B) are first reacted with each mole of polydimethylsiloxane (A), the preferred molar ratio of component (B) to component (A) being 2:1 to 7:1. The reaction is conducted under an inert atmosphere, such as nitrogen or argon and is carried out in the presence of an equilibrating amount of catalyst (C). The term "equilibrating amount" as used herein denotes a sufficient amount of acid catalyst (C) to efficiently rearrange the siloxane bonds of reactants (A) and (B) so as to provide a substantially equilibrated product of reaction within 3-5 hours at temperatures between 60 and 80°C. This amount may readily be determined by those skilled in the art by following the disappearance of the reactants using, e.g., gas chromatography, the acid being neutralized before each such determination. Thus, for example, when the catalyst is the preferred perfluoromethane sulfonic acid, it is employed at 0.04 to 0.1 weight percent of the total of components (A) and (B). This amount of perfluoromethane sulfonic acid is sufficient to equilibrate the above mentioned components within 4 hours at 70°C.

After equilibration of components (A) and (B) is attained, the reaction product is hydrolyzed with sufficient water to provide from about 0.48 to about 0.81 moles of residual alkoxy functionality per 100 parts by weight of liquid silicone resin. As should be apparent to the skilled artisan, the molar units and weight units must, of course, be consistent (e.g., gram-moles and grams, respectively). The basic reactions relied upon to calculate the amounts of water to be used in the hydrolysis step are: (i) the hydrolysis of methoxy groups on the above described equilibrated product to form silanol groups; and (ii) condensation of the silanol groups to form siloxane bonds. The net effect of these reactions, assuming the complete condensation of all silanol groups formed, requires the employment of one half mole of water for the hydrolysis of each mole of methoxy groups. Using this assumption, in combination with the above mentioned range of the ratio of the polydimethylsiloxane to the methyltrialkoxysilane, one skilled in the art can readily calculate the approximate amounts of the ingredients to be used in forming the liquid silicone resin compositions having from 0.48 to 0.81 moles of residual alkoxy functionality per 100 parts by weight of said liquid silicone resin. In practice, it has been found that the calculated (i.e., theoretical) methoxy content is generally within approximately 10 percent of the analytically determined value thereof. Preferably, the final liquid silicone resin according to the present invention has from 0.55 to 0.71 moles of residual alkoxy functionality per 100 parts by weight of the resin, a value of about 0.68 being most preferred. The hydrolysis step may be carried out at temperatures between 18 and 70°C., but preferably below the boiling point of the alcohol (e.g., MeOH) formed during the hydrolysis. This reaction should be carried out for at least one hour, whereupon the reactants are preferably heated to reflux and the alcohol formed is removed by distillation.

Finally, the acid catalyst is neutralized and the product stripped under vacuum to remove the remaining alcohol byproduct as well as other impurities. The product is then cooled and filtered.

In an alternate procedure, the compositions of the present invention may be prepared by simultaneously equilibrating and hydrolyzing components (A) and (B) in the presence of acid catalyst (C). In this case, these three components are mixed with sufficient water of hydrolysis to, again, provide from 0.48 and 0.81 moles of residual alkoxy functionality per 100 parts by weight of said liquid silicone resin. The reaction conditions as well as proportions are the same as those described above. After the reaction is completed, the acid catalyst is again neutralized and the product stripped of impurities and filtered. The resins obtained by this procedure have been found to be essentially the same as those produced by the above described two-step process with respect to residual alkoxy functionality and molecular weight distribution.

As stated above, the actual amount of residual alkoxy left on the liquid silicone resin has been found to

be critical in formulating the compositions of the present invention. For example, when less than 0.48 moles of residual methoxy functionality per 100 parts by weight of the liquid silicone resin remains (corresponding to 15 weight percent methoxy), the compositions tend to gel upon storage under ordinary conditions. On the other hand, when the methoxy content is above 0.81 moles of residual alkoxy functionality per 100 parts by weight of said liquid silicone resin (corresponding to 25 weight percent methoxy), the compositions have such a low molecular weight that they volatilize when subjected to the elevated temperatures often employed in curing such coatings on substrates. Thus, even though other useful liquid resins may result from the substitution of different diorganopolysiloxanes, such as phenylmethylpolysiloxane and trifluoropropylpolysiloxane, for the instant polydimethylsiloxanes and the substitution of different alkoxy silanes, such as ethyltrimethoxysilane and phenyltrimethoxysilane, for the instant methyltrialkoxysilanes, these resin systems fall outside the scope of the present invention. Additionally, cured films produced from such compositions are quite brittle and tend to crack easily during, or after, the cure cycle.

Because the compositions of the present invention contain residual alkoxy functionality, they may be cured by exposure to atmospheric moisture. The cure may be hastened by the addition of catalysts known in the art to promote the hydrolysis of the alkoxy groups and their subsequent condensation to form a three-dimensional siloxane network. Catalysts suitable for this purpose may be selected from the organo titanates, such as tetraisopropyl titanate and tetrabutyl titanate and organotin compounds, such as dibutyltin dilaurate, tin octoate and dibutyltin diacetate.

In addition to the above mentioned cure catalysts, the liquid silicone resin compositions may be blended with linear polydimethylsiloxanes of the type recited in the description of component (A). Addition of about 0.5 to 10 percent by weight of a polydimethylsiloxane having a viscosity of 100 to 50,000 mm²/s (cS) at 25°C. to the liquid silicone resins of the present invention results in compositions which exhibit reduced coefficients of friction (i.e., slip) and improved release when coated and cured on a substrate. The preferred polydimethylsiloxanes have a viscosity of about 1,000 to 20,000 mm²/s (cS) at 25°C. and are preferably added to the liquid silicone resins of the present invention at a level of about 1 to 2 weight percent.

The liquid resin compositions may also be blended with organic solvent solutions of solid silicone resins comprising MeSiO_{3/2}, Me₂SiO_{2/2}, PhSiO_{3/2} and Ph₂SiO_{2/2} units, wherein Ph hereinafter denotes a phenyl group. Such resins generally contain residual hydroxyl groups and are well known in the art. They are typically prepared by hydrolyzing the respective chlorosilanes in an aromatic solvent. When such modified compositions are coated onto a substrate and the solvent is evaporated, the coatings are generally clear, depending on the particular solid resin selected and its proportion. Such blended coating compositions offer advantages over the solid silicone resins in that they require lower organic solvent contents and may be cured at reduced temperatures to provide films having improved hardness.

The compositions of the present invention may further be compounded with various fillers, such as titanium dioxide and aluminum flake, pigments, thermal stabilizers and flow agents.

The present invention also relates to the above described processes used to make the liquid silicone resin compositions based on polydimethylsiloxane (A) and methyltrialkoxysilane (B).

The liquid silicone resin compositions of the present invention find utility in the preparation of protective coatings for metal, glass and plastic substrates, high temperature paints, release coatings for bakeware, binders for masonry water repellant and as a paper or fabric saturant in the manufacture of automotive gaskets, inter alia.

The following examples are presented to further illustrate the compositions of the present invention, but are not to be construed as limiting the invention, which is delineated in the appended claims. All parts and percentages in the examples are on a weight basis unless indicated to the contrary and reported viscosities were obtained at 25°C.

Examples 1 - 15

A three-neck flask, equipped with a stirrer, condenser, nitrogen purge and thermometer was charged with 820 grams (6.02 moles) of methyltrimethoxysilane and 145 grams (1.96 moles) of a mixture of polycyclosiloxanes having the formula (Me₂SiO)_x, wherein Me hereinafter denotes a methyl radical and x had a value between 3 and 10. The mixture was stirred and 0.05% (based on total silicone) of trifluoromethane sulfonic acid (0.48 gram) was added, resulting in a bright yellow color. The catalyzed mixture was then slowly heated to 70°C. and stirred at this temperature for about 4 hours, whereupon the color faded somewhat to a "light straw" appearance. The contents of the flask were allowed to cool to 52°C. and 100 grams (5.56 moles) of deionized water were added over a period of about 2 minutes. The resulting exothermic reaction brought the temperature of the mixture to about 70°C. Stirring was continued for about another hour without further application of heat. Powdered calcium carbonate (0.9 grams) was added to neutralize the acid catalyst and a vacuum (about 30

mm Hg, 3990 Pa) was applied while slowly heating to about 120°C. This temperature was held for about 15 minutes to strip off volatiles. Upon cooling and filtering the residue, 658 grams of product was recovered (92.6% yield).

In a similar manner, the compositions shown in Table 1 were prepared. In addition to the actual amounts of the reactants used (reported in the second through the fourth columns), this table shows analytical results obtained on the products: molar methyl to dimethyl ratio (Me/Me₂); weight percent methoxy (OMe); and initial viscosity mm²/s.

Table 1

Example	MeSi(OMe) ₃ (grams)	(Me ₂ SiO) _x (grams)	Water (grams)	Actual Mole Ratio Me/Me ₂	Actual Methoxy $\frac{\text{g-mol.}}{100 \text{ g resin}}$ (Wt. %)	Viscosity (mm ² /s @ 25°C.)
1	820	145	100	2.87	21.1	30
2	760	50	100	6.80	21.1	42
3	820	50	115	8.20	20.5	55
4	760	145	115	2.70	15.1	70
5	820	240	115	1.80	16.1	35
6	760	240	100	1.70	17.4	40
7	700	145	100	2.60	17.4	50
8	760	145	115	2.30	15.0	70
(Comparative) Example						
9	760	145	115	2.75	14.5	90
10	760	240	130	1.61	9.1	340
11	700	50	115	6.97	14.5	200
12	760	50	130	7.60	12.8	7,000
13	700	145	130	2.50	10.0	1,250
14	820	145	130	2.90	13.8	124
15	700	240	115	1.60	11.0	120

The liquid resin compositions of the present invention were stable when stored in sealed containers at room

temperature for more than a year whereas the comparative compositions, prepared by the same methods, tended to gel on standing, as indicated in Table 2.

5

Table 2

	(Comparative) <u>Example</u>	<u>Gel Time</u>
10	9	Less than 12 months
	10	30 Days
	11	56 Days
	12	12 Days
15	13	30 Days
	14	9 Months
	15	9 Months

20

(Comparative) Example 16

A procedure similar to that used to prepare Example 1 was followed in the preparation of a composition having a theoretical Me/Me₂ mole ratio of 3:1 and a theoretical methoxy functionality of 34.2% (i.e., 154 grams of polycyclosiloxanes, 846 grams of methyltrimethoxysilane and 68.5 grams water). After the stripping step, the amount of liquid resin obtained was only 52% of the theoretical value.

The above liquid resin was coated onto a steel panel and a cure at 150°C. for 30 minutes was attempted, whereupon all the material on the panel volatilized, an indication of its low molecular weight.

Adding 10% of tetraisopropyl titanate (hereinafter TIPT) to the above liquid resin, coating this mixture onto a steel panel and curing at 150°C. for 30 minutes, resulted in a film which cracked profusely when the panel had cooled to room temperature, indicating the film's brittle nature.

Example 17

A procedure similar to that used to prepare (Comparison) Example 16 was followed wherein the theoretical values of the Me/Me₂ ratio and percent methoxy functionality were 2.95 and 19.3%, respectively. The yield of the liquid resin from this preparation was 73.7% while the actual values of Me/Me₂ and methoxy were 2.89 and 18.3%, respectively. The latter value corresponds to 0.590 moles methoxy/100 g resin.

The above liquid resin was catalyzed with 0.2% of TIPT, coated onto a steel panel and cured at 150°C. for 30 minutes. The coating was soft and easily scratched. After an additional 30 minutes at 150°C., the coating, which was between 0.01 and 0.025 mm (0.4 and 1.0 mil) thick, had a pencil hardness of F to 4H. The pencil hardness was determined by attempting to scratch the cured coating surface with a sharp pencil, the reported value being the designation of the hardest pencil which would not scratch the surface (ASTM Test Method D 3363).

45

Example 18

Portions of the liquid resin of Example 1 were mixed with the catalysts shown in Table 3, wherein TBT and DBTDA hereinafter denote tetra(n-butyl) titanate and dibutyltin diacetate, respectively. These catalyzed compositions were then flow-coated onto clean steel panels and, after being hung vertically at room temperature for 24 hours to dry, the coatings were cured at 93.3°C (200°F) for 30 minutes.

In addition to the determination of pencil hardness, these coatings were subjected to a slip test which provided an indication of their coefficient of friction. This test basically consisted of placing a gauze-covered weight (100 grams) on the coated panel and tilting the panel. The angle of incline (from the horizontal) at which this weight started to slide was designated as the "slip angle" and is also reported in Table 3.

55

Table 3

Catalyst Employed	Catalyst Amount (%)	Coating Thickness mm (Mils)	Pencil Hardness	Slip Angle (Degrees)
TBT	5	(0.39)0.0098	F	8
TBT	5	(0.37)0.0094	F	8
TIPT	2	(0.37)0.0094	H	8
TIPT	2	(0.41)0.0104	H	8
DBTDA	5	(0.31)0.0079	2B	7
DBTDA	5	(0.30)0.0076	2B	7

When zinc octoate and aluminum acetylacetonate were used as catalysts at a 2% level, the coatings did not cure under the above describe conditions.

Example 19

A liquid resin similar to Example 1, having a Me/Me₂ ratio of 2.6 and a methoxy content of 20.4%, was used to prepare a paint having an equal weight of TiO₂ powder based on the resin solids content. Mica (325 mesh) was also added to this paint formulation at a level of about 32% based on the TiO₂ content. The mixing was accomplished with a laboratory mixer having Cowles blades (3600 r.p.m. for 25 minutes) to obtain a uniform dispersion. Portions of this filled system were catalyzed as shown in Table 4, below. These compositions were brushed onto steel panels and cured at 204°C (400°F). for 30 minutes. After being cured, the panels were aged

in an air oven at 260°C (500°F). and pencil hardness values were determined at various times, as shown in Table 4.

Table 4

Amount of TBT Catalyst Added (%)	Pencil Hardness After Aging at 260°C (500°F).				
	Initial	200 Hours	500 Hours	800 Hours	1,000 Hours
None	B	HB	HB	HB	HB
0.5	2B	HB	B	4B	2B
1.0	HB	2B	4B	4B	2B

From the above table it is seen that the titanium dioxide-filled coatings of the present invention are resistant to thermal and oxidative degradation, particularly when no catalyst is added.

Example 20

Two parts of the above liquid resin of Example 19 were mixed with one part of E-30 flaked aluminum (Reynolds Metals Company, Richmond, VA) on a mixing wheel for one hour. The coating composition containing the aluminum flake was filtered and sprayed onto steel panels, held at room temperature for 15 minutes and cured at 232°C (450°F). for 30 minutes. Initial pencil hardness of the film, which had a thickness of 0,024 +/-

0,007 mm (0.96 +/- 0.27 mil), was F. After 24 hours aging at 538°C (1,000°F.), the hardness increased to above 9H. The film survived 1,000 hours at 538°C (1,000°F.) without flaking off the panel.

5 Example 21

A liquid resin similar to Example 1, having a Me/Me₂ ratio of 3.2 and a methoxy content of 22.9%, was thoroughly mixed with 1% of a trimethylsilyl endblocked linear polydimethylsiloxane having a viscosity of 12,500 (cS). mm²/s Portions of this composition were catalyzed with TBT, coated onto steel panels and cured, as indicated in Table 5, below.

Table 5

Amount of TBT (%)	Cure Temp./ Cure Time	Film Thickness (Mil) mm	Pencil Hardness	Slip Angle (degrees)
1	149°C(300°F)/30 min.	(0.35 +/- 0.10) 0,0089±0,0025	2B	10
1	218,5°C(425°F)/60 min.	(0.08 +/- 0.03) 0,002±0,0008	5H	6
0.5	218,5°C(425°F)/60 min.	(0.03 +/- 0.02) 0,0008±0,0005	5H	4

Example 22

5 A liquid resin similar to Example 1, having a Me/Me₂ ratio of 2.6 and a methoxy content of 20.4%, was mixed with 9% of a hydroxy-endblocked polydimethylsiloxane having a viscosity of about 70 (cS) mm²/s and catalyzed with 0.2% DBTDA plus 0.2% TIPT. After this composition was coated onto a steel panel and cured at 149°C (300°F) for 50 minutes followed by 204°C (400°F) for 10 minutes, the resulting film had a thickness of 0,021 ± 0,005 mm (0.83 +/- 0.19 mil), a pencil hardness of F and a slip angle of 8 degrees. Although as much as 44% of the above mentioned hydroxy-endblocked polydimethylsiloxane could be blended with the liquid resin compositions of the present invention without haze formation (i.e., the mixtures were clear and stable), coatings having more than about 9% were considerably softer.

10 The above two examples illustrates the compatibility of polydimethylsiloxane fluids with the liquid resin compositions of the present invention and show the utility of the instant compositions in the formation of coatings having improved slip or release properties.

15

Example 23

20 A liquid resin similar to Example 1, having a Me/Me₂ ratio of 3.2 and a methoxy content of 22.9%, was mixed with equal weights of solutions of three different silicone resins comprising MeSiO_{3/2}, Me₂SiO_{2/2}, PhSiO_{3/2} and Ph₂SiO_{2/2} units, wherein Ph hereinafter denotes a phenyl group (Table 6). These resins were prepared by hydrolyzing the respective chlorosilanes in the indicated aromatic solvent and they had the molar compositions and weight percent of residual hydroxyl functionality shown in Table 6, below. These compositions were coated onto steel panels and cured at 204°C (400°F) for 35 minutes followed by 260°C (500°F) for 10 minutes.

25

30

35

40

45

50

55

Table 6

Resin Composition (Mole Ratio) (MeSiO _{3/2} :Me ₂ SiO _{2/2} : PhSiO _{3/2} :Ph ₂ SiO _{2/2})	Percent OH on Resin (As SiOH)	Coating Thickness mm(Mil)	Hardness	Slip Angle (Degrees)
32:29:39:0 (a)	3	(0.35 +/- 0.07) 0.0089 ± 0.0018	2H	17
15:40:35:10 (b)	1	(0.30 +/- 0.04) 0.0076 ± 0.0010	B	>30
25:19:37:19 (a)	3	(0.29 +/- 0.04) 0.0074 ± 0.0010	H	10

(a) Solution consisted essentially of 60% resin solids in toluene.

(b) Solution consisted essentially of 50% resin solids in xylene.

The above results illustrate the ease with which the compositions of the present invention may be blended with conventional phenyl-containing silicone resins to yield clear films, which films had good adhesion to the metal substrate.

Examples 24 - 25

A binder resin was prepared as described in Example 8 of United States Patent No. 4,113,665 to Law et al. (Comparative Example 24). In this comparative example, 855 grams of methyltrimethoxysilane was reacted with 108 grams of a hydroxyl functional silicone intermediate of the type used by Law et al. This intermediate

is a 60% solids solution of a silanol-functional resin having $\text{MeSiO}_{3/2}$, $\text{Me}_2\text{SiO}_{2/2}$, $\text{PhSiO}_{3/2}$ and $\text{Ph}_2\text{SiO}_{2/2}$ units in a molar ratio of 25:20:35:20 having a hydroxyl content of about 3%. The methyltrimethoxysilane was hydrolyzed with 126 grams of 15% aqueous phosphoric acid, as stipulated in said patent example. Thus, the weight ratio of methyltrimethoxysilane to the silicone intermediate, on a solids basis, was about 13. No fillers were added to this binder composition.

A composition according to the present invention (Example 25) was prepared using the same weight ratio of methyltrimethoxysilane to the above described mixture of polycyclosiloxanes (i.e., a ratio of 13, as in the case of the above cited patent to Law et al.). This composition had a Me/Me_2 ratio of 7.1 and a methoxy content of 23%.

A comparison of the above two compositions is shown in Table 7, wherein analytical and cured film properties are reported.

Table 7

	(Comparative) Example 24 (Law et al. patent)	Example 25 (This Invention)
Me/Me ₂ Ratio (Molar)	37	7.1
Methoxy (Wt. %)	37	23
No. Avg. Molecular Weigh (by g.p.c.)	3,300	980
Wt. Avg. Molecular Weight (by g.p.c.)	590,000	66,000
Weight Loss (250°C./3 hours)	11.7%	38.2%
Viscosity (cS) mm ² /s	3	9
Closed Cup Flash Pt.	(46°F) 7,8°C	(194°F) 90°C
<u>Film Properties (1% TBT catalyst added in each case)</u>		
Pencil Hardness (Room Temp. Cure)	Softer than 6B	B
(Cure @ 149°C (300°F). / 30 min.)	Softer than 6B	2H
Slip Angle (Degrees) (Room Temp. Cure)	>35	10
(Cure @ 149°C (300°F). / 30 min.)	>35	8

Claims

1. A liquid silicone resin composition prepared by a process comprising:

(I) reacting a mixture consisting essentially of

(A) a polydimethylsiloxane, wherein optionally up to 10 mole percent of siloxane units may contain alkyl groups having 2 to 8 carbon atoms, phenyl groups or trifluoropropyl groups,

(B) a methyltrialkoxysilane having the formula $\text{MeSi}(\text{OR})_3$, wherein Me denotes a methyl radical and R is an alkyl radical having from 1 to 3 carbon atoms, and

(C) an equilibrating amount of an acid catalyst having the formula $\text{R}'\text{SO}_3\text{H}$ wherein R' is a perfluoroalkyl group having 1 to 10 carbon atoms, the molar ratio of said methyltrialkoxysilane (B) to said

- polydimethylsiloxane (A) being between 1:1 and 10:1;
 (II) hydrolyzing the reaction product formed in step (I) with sufficient water to provide from 0.48 to 0.81 mole of residual alkoxy functionality per 100 parts by weight of said liquid silicone resin; and
 5 (III) neutralizing said acid catalyst (C).
2. The composition according to claim 1, comprising the further addition of from about 0.5 to 10 weight percent of a linear polydimethylsiloxane (E) having a viscosity of about 100 to 50,000 mm²/s (cS) at 25°C.
- 10 3. The composition according to claim 1, comprising the further addition of a solid silicone resin containing siloxane units selected from the group consisting of MeSiO_{3/2}, Me₂SiO_{2/2}, PhSiO_{3/2} and Ph₂SiO_{2/2} units, wherein Me and Ph denote methyl and phenyl groups, respectively.
4. A liquid silicone resin composition prepared by a process comprising:
 15 (I) reacting a mixture consisting essentially of
 (A) a polydimethylsiloxane, wherein optionally up to 10 mole percent of siloxane units may contain alkyl groups having 2 to 8 carbon atoms, phenyl groups or trifluoropropyl groups,
 (B) a methyltrialkoxysilane having the formula MeSi(OR)₃, wherein Me denotes a methyl radical and R is an alkyl radical having from 1 to 3 carbon atoms,
 20 (C) an equilibrating amount of an acid catalyst having the formula R'SO₃H wherein R' is a perfluoroalkyl group having 1 to 10 carbon atoms, the molar ratio of said methyltrialkoxysilane (B) to said polydimethylsiloxane (A) being between 1:1 and 10:1, and
 (D) sufficient water of hydrolysis to provide from 0.48 to 0.81 mole of residual alkoxy functionality per 100 parts by weight of said liquid silicone resin; and
 25 (II) neutralizing said acid catalyst (C).
5. The composition according to claim 4, comprising the further addition of from about 0.5 to 10 weight percent of a linear polydimethylsiloxane (E) having a viscosity of about 100 to 50,000 mm²/s (cS) at 25°C.
- 30 6. The composition according to claim 4, comprising the further addition of a solid silicone resin containing siloxane units selected from the group consisting of MeSiO_{3/2}, Me₃SiO_{2/2}, PhSiO_{3/2} and Ph₂SiO_{2/2} units, wherein Me and Ph denote methyl and phenyl groups, respectively.
7. A process for preparing a liquid silicone resin composition comprising:
 35 (I) reacting a mixture consisting essentially of
 (A) a polydimethylsiloxane, wherein optionally up to 10 mole percent of siloxane units may contain alkyl groups having 2 to 8 carbon atoms, phenyl groups or trifluoropropyl groups,
 (B) a methyltrialkoxysilane having the formula MeSi(OR)₃, wherein Me denotes a methyl radical and R is an alkyl radical having from 1 to 3 carbon atoms, and
 40 (C) an equilibrating amount of an acid catalyst having the formula R'SO₃H wherein R' is a perfluoroalkyl group having 1 to 10 carbon atoms, the molar ratio of said methyltrialkoxysilane (B) to said polydimethylsiloxane (A) being between 1:1 and 10:1;
 (II) hydrolyzing the reaction product formed in step (I) with sufficient water to provide from 0.48 to 0.81 mole of residual alkoxy functionality per 100 parts by weight of said liquid silicone resin; and
 45 (III) neutralizing said acid catalyst (C).
8. A process for preparing a liquid silicone resin composition comprising:
 50 (I) reacting a mixture consisting essentially of
 (A) a polydimethylsiloxane, wherein optionally up to 10 mole percent of siloxane units may contain alkyl groups having 2 to 8 carbon atoms, phenyl groups or trifluoropropyl groups,
 (B) a methyltrialkoxysilane having the formula MeSi(OR)₃, wherein Me denotes a methyl radical and R is an alkyl radical having from 1 to 3 carbon atoms,
 55 (C) an equilibrating amount of an acid catalyst having the formula R'SO₃H wherein R' is a perfluoroalkyl group having 1 to 10 carbon atoms, the molar ratio of said methyltrialkoxysilane (B) to said polydimethylsiloxane (A) being between 1:1 and 10:1, and
 (D) sufficient water of hydrolysis to provide from 0.48 to 0.81 mole of residual alkoxy functionality per 100 parts by weight of said liquid silicone resin; and
 (II) neutralizing said acid catalyst (C).

Patentansprüche

1. Flüssige Silikonharzzusammensetzung, hergestellt mit einem Verfahren, umfassend, daß man:
 - (I) eine Mischung, die im wesentlichen aus
 - (A) einem Polydimethylsiloxan, worin gegebenenfalls bis zu 10 Mol-% Siloxaneinheiten Alkylgruppen mit 2 bis 8 Kohlenstoffatomen, Phenylgruppen oder Trifluorpropylgruppen enthalten können,
 - (B) einem Methyltrialkoxysilan mit der Formel $\text{MeSi}(\text{OR})_3$, worin Me einen Methylrest bezeichnet und R ein Alkylrest mit 1 bis 3 Kohlenstoffatomen ist, und
 - (C) einer equilibrierenden Menge eines sauren Katalysators der Formel $\text{R}'\text{SO}_3\text{H}$, worin R' eine Perfluoralkylgruppe mit 1 bis 10 Kohlenstoffatomen ist,
 besteht, umsetzt, wobei das molare Verhältnis von Methyltrialkoxysilan (B) zu Polydimethylsiloxan (A) zwischen 1:1 und 10:1 liegt;
 - (II) das in Stufe (I) gebildete Reaktionsprodukt mit ausreichend Wasser hydrolysiert, um 0,48 bis 0,81 Mol restliche Alkoxyfunktionen pro 100 Gew.-Teile des flüssigen Silikonharzes zu schaffen, und
 - (III) den sauren Katalysator (C) neutralisiert.
2. Zusammensetzung nach Anspruch 1, worin weiterhin etwa 0,5 bis 10 Gew.-% eines linearen Polydimethylsiloxans (E) mit einer Viskosität von etwa 100 bis 50 000 mm²/s (cS) bei 25°C zugegeben werden.
3. Zusammensetzung nach Anspruch 1, worin weiterhin ein festes Silikonharz, das Siloxaneinheiten ausgewählt aus der Gruppe bestehend aus $\text{MeSiO}_{3/2}$ -, $\text{Me}_2\text{SiO}_{2/2}$ -, $\text{PhSiO}_{3/2}$ - und $\text{Ph}_2\text{SiO}_{2/2}$ -Einheiten, worin Me und ph Methyl- bzw. Phenylgruppen bedeuten, enthält, zugegeben wird.
4. Flüssige Silikonharzzusammensetzung, hergestellt mit einem Verfahren, umfassend, daß man:
 - (I) eine Mischung, die im wesentlichen aus
 - (A) einem Polydimethylsiloxan, worin gegebenenfalls bis zu 10 Mol-% Siloxaneinheiten Alkylgruppen mit 2 bis 8 Kohlenstoffatomen, Phenylgruppen oder Trifluorpropylgruppen enthalten können,
 - (B) einem Methyltrialkoxysilan der Formel $\text{MeSi}(\text{OR})_3$, worin Me einen Methylrest bezeichnet und R ein Alkylrest mit 1 bis 3 Kohlenstoffatomen ist,
 - (C) einer equilibrierenden Menge eines sauren Katalysators der Formel $\text{R}'\text{SO}_3\text{H}$, worin R' eine Perfluoralkylgruppe mit 1 bis 10 Kohlenstoffatomen ist, wobei das molare Verhältnis von Methyltrialkoxysilan (B) zu Polydimethylsiloxan (A) zwischen 1:1 und 10:1 liegt, und
 - (D) ausreichend Wasser für die Hydrolyse, um 0,48 bis 0,81 Mol restliche Alkoxyfunktionen pro 100 Gew.-Teile flüssiges Silikonharz zu liefern,
 besteht, umsetzt, und
 - (II) den sauren Katalysator (C) neutralisiert.
5. Zusammensetzung nach Anspruch 4, worin weiterhin etwa 0,5 bis 10 Gew.-% eines linearen Polydimethylsiloxans (E) mit einer Viskosität von etwa 100 bis 50 000 mm²/s (cS) bei 25°C zugegeben werden.
6. Zusammensetzung nach Anspruch 4, worin weiterhin ein festes Silikonharz, das Siloxaneinheiten ausgewählt aus der Gruppe bestehend aus $\text{MeSiO}_{3/2}$ -, $\text{Me}_2\text{SiO}_{2/2}$ -, $\text{PhSiO}_{3/2}$ - und $\text{Ph}_2\text{SiO}_{2/2}$ -Einheiten, worin Me und Ph Methyl- bzw. Phenylgruppen bedeuten, enthält, zugegeben wird.
7. Verfahren zur Herstellung einer flüssigen Silikonharzzusammensetzung, umfassend, daß man:
 - (I) eine Mischung, die im wesentlichen aus
 - (A) einem Polydimethylsiloxan, worin gegebenenfalls bis zu 10 Mol-% Siloxaneinheiten Alkylgruppen mit 2 bis 8 Kohlenstoffatomen, Phenylgruppen oder Trifluorpropylgruppen enthalten können,
 - (B) einem Methyltrialkoxysilan mit der Formel $\text{MeSi}(\text{OR})_3$, worin Me einen Methylrest bezeichnet und R ein Alkylrest mit 1 bis 3 Kohlenstoffatomen ist, und
 - (C) einer equilibrierenden Menge eines sauren Katalysators der Formel $\text{R}'\text{SO}_3\text{H}$, worin R' eine Perfluoralkylgruppe mit 1 bis 10 Kohlenstoffatomen ist,
 besteht, umsetzt, wobei das molare Verhältnis von Methyltrialkoxysilan (B) zu Polydimethylsiloxan (A) zwischen 1:1 und 10:1 liegt;
 - (II) das in Stufe (I) gebildete Reaktionsprodukt mit ausreichend Wasser hydrolysiert, um 0,48 bis 0,81 Mol restliche Alkoxyfunktionen pro 100 Gew.-Teile des flüssigen Silikonharzes zu schaffen, und
 - (III) den sauren Katalysator (C) neutralisiert.
8. Verfahren zur Herstellung einer flüssigen Silikonharzzusammensetzung, umfassend, daß man:

(I) eine Mischung, die im wesentlichen aus

(A) einem Polydimethylsiloxan, worin gegebenenfalls bis zu 10 Mol-% Siloxaneinheiten Alkylgruppen mit 2 bis 8 Kohlenstoffatomen, Phenylgruppen oder Trifluorpropylgruppen enthalten können,

(B) einem Methyltrialkoxysilan der Formel $\text{MeSi}(\text{OR})_3$, worin Me einen Methylrest bezeichnet und R ein Alkylrest mit 1 bis 3 Kohlenstoffatomen ist,

(C) einer equilibrierenden Menge eines sauren Katalysators der Formel $\text{R}'\text{SO}_3\text{H}$, worin R' eine Perfluoralkylgruppe mit 1 bis 10 Kohlenstoffatomen ist, wobei das molare Verhältnis von Methyltrialkoxysilan (B) zu Polydimethylsiloxan (A) zwischen 1:1 und 10:1 liegt, und

(D) ausreichend Wasser für die Hydrolyse, um 0,48 bis 0,81 Mol restliche Alkoxyfunktionen pro 100 Gew.-Teile flüssiges Silikonharz zu liefern,

besteht, umgesetzt, und

(II) den sauren Katalysator (C) neutralisiert.

Revendications

1. Une composition de résine de silicone liquide préparée par un procédé comprenant les opérations consistant :

(I) à faire réagir un mélange essentiellement constitué

(A) d'un polydiméthylsiloxane, dans lequel facultativement jusqu'à 10 moles pour cent de motifs siloxanes peuvent porter des groupes alkyles comptant 2 à 8 atomes de carbone, des groupes phényle ou des groupes trifluoropropyle,

(B) d'un méthyltrialcoxysilane de formule $\text{MeSi}(\text{OR})_3$, où Me représente un radical méthyle et R est un radical alkyle comptant 1 à 3 atomes de carbone, et

(C) d'une quantité équilibrante d'un catalyseur acide de formule $\text{R}'\text{SO}_3\text{H}$, dans laquelle R' est un groupe perfluoroalkyle comptant 1 à 10 atomes de carbone, le rapport molaire dudit méthyltrialcoxysilane (B) audit polydiméthylsiloxane (A) étant compris entre 1:1 et 10:1;

(II) à hydrolyser le produit de réaction formé à l'opération (I) avec suffisamment d'eau pour obtenir 0,48 à 0,81 mole de fonctionnalité alcoxy résiduelle pour 100 parties en poids de ladite résine de silicone liquide; et

(III) à neutraliser ledit catalyseur acide (C).

2. La composition selon la revendication 1, comprenant l'addition supplémentaire d'environ 0,5 à 10 pour cent en poids d'un polydiméthylsiloxane linéaire (E) présentant une viscosité à 25°C d'environ 100 à 50000 mm²/s.

3. La composition selon la revendication 1, comprenant l'addition supplémentaire d'une résine de silicone solide contenant des motifs siloxanes choisis dans le groupe formé par les motifs $\text{MeSiO}_{3/2}$, $\text{Me}_2\text{SiO}_{2/2}$, $\text{PhSiO}_{3/2}$ et $\text{Ph}_2\text{SiO}_{2/2}$, où Me et Ph désignent respectivement des groupes méthyle et phényle.

4. Une composition de résine de silicone liquide préparée par un procédé comprenant les opérations consistant :

(I) à faire réagir un mélange essentiellement constitué

(A) d'un polydiméthylsiloxane, dans lequel facultativement jusqu'à 10 moles pour cent de motifs siloxanes peuvent contenir des groupes alkyles comptant 2 à 8 atomes de carbone, des groupes phényle ou des groupes trifluoropropyle,

(B) d'un méthyltrialcoxysilane de formule $\text{MeSi}(\text{OR})_3$, où Me représente un radical méthyle et R est un radical alkyle comptant 1 à 3 atomes de carbone,

(C) d'une quantité équilibrante d'un catalyseur acide de formule $\text{R}'\text{SO}_3\text{H}$, dans laquelle R' est un groupe perfluoroalkyle comptant 1 à 10 atomes de carbone, le rapport molaire dudit méthyltrialcoxysilane (B) audit polydiméthylsiloxane (A) étant compris entre 1:1 et 10:1, et

(D) de suffisamment d'eau d'hydrolyse pour obtenir 0,48 à 0,81 mole de fonctionnalité alcoxy résiduelle pour 100 parties en poids de ladite résine de silicone liquide; et

(II) à neutraliser ledit catalyseur acide (C).

5. La composition selon la revendication 4, comprenant l'addition supplémentaire d'environ 0,5 à 10 pour cent en poids d'un polydiméthylsiloxane linéaire (E) présentant une viscosité à 25°C d'environ 100 à 50 000 mm²/s.

6. La composition selon la revendication 4, comprenant l'addition supplémentaire d'une résine de silicone solide contenant des motifs siloxanes choisis dans le groupe formé par les motifs $\text{MeSiO}_{3/2}$, $\text{Me}_2\text{SiO}_{2/2}$, $\text{PhSiO}_{3/2}$ et $\text{Ph}_2\text{SiO}_{2/2}$, où Me et Ph désignent respectivement des groupes méthyle et phényle.

7. Un procédé pour la préparation d'une composition de résine de silicone liquide comprenant les opérations consistant :

(I) à mettre en réaction un mélange essentiellement constitué

(A) d'un polydiméthylsiloxane, dans lequel facultativement jusqu'à 10 moles pour cent de motifs siloxanes peuvent contenir des groupes alkyles comptant 2 à 8 atomes de carbone, des groupes phényle ou des groupes trifluoropropyle,

(B) d'un méthyltrialcoxysilane de formule MeSi(OR)_3 , où Me représente un radical méthyle et R est un radical alkyle comptant 1 à 3 atomes de carbone, et

(C) d'une quantité équilibrante d'un catalyseur acide de formule $\text{R'SO}_3\text{H}$, dans laquelle R' est un groupe perfluoroalkyle comptant 1 à 10 atomes de carbone, le rapport molaire dudit méthyltrialcoxysilane (B) audit polydiméthylsiloxane (A) étant compris entre 1:1 et 10:1;

(II) à hydrolyser le produit de réaction formé à l'opération (I) avec suffisamment d'eau pour obtenir 0,48 à 0,81 mole de fonctionnalité alcoxy résiduelle pour 100 parties en poids de ladite résine de silicone liquide; et

(III) à neutraliser ledit catalyseur acide (C).

8. Un procédé pour la préparation d'une composition de résine de silicone liquide comprenant les opérations consistant :

(I) à mettre en réaction un mélange essentiellement constitué

(A) d'un polydiméthylsiloxane, dans lequel facultativement jusqu'à 10 moles pour cent de motifs siloxanes peuvent porter des groupes alkyles comptant 2 à 8 atomes de carbone, des groupes phényle ou des groupes trifluoropropyle,

(B) d'un méthyltrialcoxysilane de formule MeSi(OR)_3 , où Me représente un radical méthyle et R est un radical alkyle comptant 1 à 3 atomes de carbone,

(C) d'une quantité équilibrante d'un catalyseur acide de formule $\text{R'SO}_3\text{H}$, dans laquelle R' est un groupe perfluoroalkyle comptant 1 à 10 atomes de carbone, le rapport molaire dudit méthyltrialcoxysilane (B) audit polydiméthylsiloxane (A) étant compris entre 1:1 et 10:1, et

(D) de suffisamment d'eau d'hydrolyse pour obtenir 0,48 à 0,81 mole de fonctionnalité alcoxy résiduelle pour 100 parties en poids de ladite résine de silicone liquide; et

(II) à neutraliser ledit catalyseur acide (C).